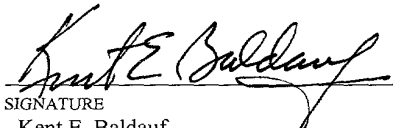


Form PTO-1390 U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE (REV 10-95)		ATTORNEY'S DOCKET NUMBER <b>1217-020321</b>
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. (if known, see 37 CFR 1.5) <b>10/070110</b>
INTERNATIONAL APPLICATION NO. <b>PCT/JP00/05334</b>	INTERNATIONAL FILING DATE <b>09.08.00 (09 August 2000)</b>	PRIORITY DATES CLAIMED <b>31.08.99 (31 August 1999)</b>
TITLE OF INVENTION <b>NOVEL ALUMINA HYDRATE PARTICLE, ALUMINA HYDRATE PARTICLE DISPERSION SOL, COATING LIQUID FOR FORMING INK RECEPTIVE LAYER AND SUBSTRATE WITH INK RECEPTIVE LAYER</b>		
APPLICANT(S) FOR DO/EO/US <b>Hiroyasu NISHIDA, Naoyuki ENOMOTO, Michio KOMATSU</b>		
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</li> <li><input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li> <li><input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))             <ol style="list-style-type: none"> <li><input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li><input checked="" type="checkbox"/> has been transmitted by the International Bureau.</li> <li><input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li><input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li><input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))             <ol style="list-style-type: none"> <li><input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li><input type="checkbox"/> have been transmitted by the International Bureau.</li> <li><input type="checkbox"/> have not been made, however, the time limit for making such amendments has NOT expired.</li> <li><input checked="" type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li><input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li><input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</li> <li><input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</li> </ol> <p><b>Items 11. to 16. below concern document(s) or information included:</b></p> <ol style="list-style-type: none"> <li><input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li><input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li><input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.              <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li><input type="checkbox"/> A substitute specification</li> <li><input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li><input checked="" type="checkbox"/> Other items or information:             <ol style="list-style-type: none"> <li>WO 01/16026-Front Page And International Search Report (3 pp.)</li> </ol> </li> </ol>		

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U.S. APPLICATION NO. (if known) <b>10/070110</b>	INTERNATIONAL APPLICATION NO. PCT/JP00/05334	ATTORNEY'S DOCKET NUMBER 1217-020321
17. <input checked="" type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):</b> Search Report has been prepared by the EPO or JPO. .... \$890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... \$710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))..... \$740.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. .... \$1040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$100.00		CALCULATIONS PTO USE ONLY
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>		<b>\$ 890.00</b>
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		<b>\$ 0.00</b>
CLAIMS	NUMBER FILED	NUMBER EXTRA
Total claims	8 - 20	0
Independent claims	5 - 3 =	2
MULTIPLE DEPENDENT CLAIM(S) (if applicable)		+ \$280.00
<b>TOTAL OF ABOVE CALCULATIONS =</b>		<b>\$ 1058.00</b>
Reduction of 1/2 for filing by small entity, if applicable. Small entity status verified by Applicants' attorney.		<b>\$ 529.00</b>
<b>SUBTOTAL =</b>		<b>\$ 529.00</b>
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +		<b>\$ 0.00</b>
<b>TOTAL NATIONAL FEE =</b>		<b>\$ 529.00</b>
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +		<b>\$ 40.00</b>
<b>TOTAL FEES ENCLOSED =</b>		<b>\$ 569.00</b>
a. <input checked="" type="checkbox"/> A check in the amount of <b>\$ 569.00</b> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-0650</u> . A duplicate copy of this sheet is enclosed		Amount to be: Refunded \$ Charged \$
<b>NOTE:</b> Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.		
SEND ALL CORRESPONDENCE TO Kent E. Baldauf 700 Koppers Building 436 Seventh Avenue Pittsburgh, Pennsylvania 15219-1818 Telephone: (412) 471-8815 Facsimile: (412) 471-4094		
<div style="text-align: right;">             SIGNATURE            Kent E. Baldauf            NAME            25,826            REGISTRATION NUMBER         </div>		

10/070110

JC19 Rec'd PCT/PTO 28 FEB 2002

PATENT APPLICATION/PCT  
Attorney Docket No. 1217-020321

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of :  
Hiroyasu NISHIDA : NOVEL ALUMINA HYDRATE PARTICLE,  
Naoyuki ENOMOTO : ALUMINA HYDRATE PARTICLE  
Michio KOMATSU : DISPERSION SOL, COATING LIQUID FOR  
FORMING INK RECEPTIVE LAYER AND  
International Application : SUBSTRATE WITH INK RECEPTIVE  
No. PCT/JP00/05334 : LAYER  
International Filing Date :  
09 August 2000 :  
Priority Date Claimed :  
31 August 1999 :  
Serial No. Not Yet Assigned :  
Filed Concurrently Herewith : Pittsburgh, Pennsylvania  
February 28, 2002

**PRELIMINARY AMENDMENT**

Box PCT  
Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to initial examination, please amend the above-identified patent application as follows:

**IN THE SPECIFICATION:**

**On page 1, please delete the section heading "DESCRIPTION".**

**Please replace the section heading beginning at page 1, line 7 with the**

**following rewritten section headings:**

**BACKGROUND OF THE INVENTION**

1. **Field of the Invention**

Please replace the section heading beginning at page 1, line 22 with the following rewritten section heading:

2. Description of the Prior Art

Please replace the paragraph beginning at page 4, line 22 with the following rewritten paragraph:

The present invention has been made with a view toward solving the above problems of the prior art. In overcoming these problems, the present invention provides alumina hydrate particles and a process for producing same wherein the particles have a large pore volume and have a pore diameter which falls in a specified range, and, in addition, provides a highly transparent alumina hydrate particle dispersion sol which, even if in a high concentration, exhibits a low viscosity.

Please replace the paragraph beginning at page 5, line 5 with the following rewritten paragraph:

The present invention further provides a coating liquid for forming an ink receptive layer wherein the above alumina hydrate particles are contained, and provides a substrate with an ink receptive layer formed with the use of the coating liquid.

Please replace the section heading beginning at page 5, line 11 with the following rewritten section heading:

SUMMARY OF THE INVENTION

Please replace the section heading beginning at page 7, line 12 with the following rewritten section heading:

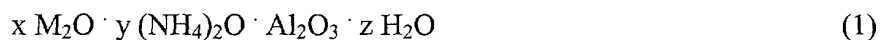
DETAILED DESCRIPTION OF THE INVENTION

On page 22, please delete the section heading "EFFECT OF THE INVENTION".

**IN THE CLAIMS:**

Please cancel claims 1-6 and insert the following new claims 7-14 as follows:

8/. Alumina hydrate particles having a composition represented by the general formula:



$$2 \times 10^{-4} \leq x \leq 25 \times 10^{-4}$$

$$0.1 \times 10^{-4} \leq y \leq 20 \times 10^{-4}$$

$$0.6 \leq z \leq 2.5$$

wherein M represents an alkali metal; when the alkali metal is in the form of  $M_2O$ , x is the number of moles thereof per mol of  $Al_2O_3$ ; when ammonia is in the form of  $(NH_4)_2O$ , y is the number of moles thereof per mol of  $Al_2O_3$ ; and z is the number of moles of hydration water ( $H_2O$ ) per mol of  $Al_2O_3$ ,

said alumina hydrate particles having:

an average particle diameter of 0.02 to 0.2  $\mu m$ ,

a total pore volume of 0.5 to 1.5 ml/g, and

a volume of pores whose diameter is from 15 to 30 nm ranging from 0.3 to 1.0 ml/g.

8. A process for producing alumina hydrate particles, comprising the steps of:

neutralizing an aqueous solution of alkali metal aluminate or an aqueous solution of aluminum salt to thereby form an alumina hydrogel;

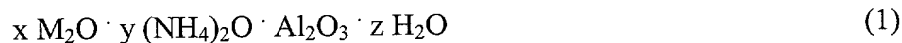
separating the alumina hydrogel by filtration, and washing the separated alumina hydrogel with water and/or aqueous ammonia;

adjusting the pH value of the washed alumina hydrogel so as to fall within the range of 9 to 12, and heating the alumina hydrogel at 50 to 105°C to thereby effect aging of the alumina hydrogel;

adding an acid to the alumina hydrogel so that the alumina hydrogel is deflocculated into an alumina hydrosol; and

drying the alumina hydrosol.

10. An alumina hydrate particle dispersion sol comprising a dispersion of alumina hydrate particles in water, wherein said alumina hydrate particles have a composition represented by the general formula:



$$2 \times 10^{-4} \leq 10^{-4} \leq x \leq 25 \times 10^{-4}$$

$$0.1 \times 10^{-4} \leq y \leq 20 \times 10^{-4}$$

$$0.6 \leq z \leq 2.5$$

wherein M represents an alkali metal; when the alkali metal is in the form of  $M_2O$ , x is the number of moles thereof per mol of  $Al_2O_3$ ; when ammonia is in the form of  $(NH_4)_2O$ , y is the number of moles thereof per mol of  $Al_2O_3$ ; and z is the number of moles of hydration water ( $H_2O$ ) per mol of  $Al_2O_3$ ,

said alumina hydrate particles having:

an average particle diameter of 0.02 to 0.2  $\mu m$ ,

a total pore volume of 0.5 to 1.5 ml/g, and

a volume of pores whose diameter is from 15 to 30 nm ranging from 0.3 to 1.0

ml/g.

11. The alumina hydrate particle dispersion sol as claimed in claim 9 having an absorbance (ABS) of 2.0 or less exhibited when the  $Al_2O_3$  has a concentration of 20% by weight.

12  
11. The alumina hydrate particle dispersion sol as claimed in claim 9 having a viscosity of 50 to 2000 cP exhibited when the  $\text{Al}_2\text{O}_3$  has a concentration of 20% by weight.

13/12. The alumina hydrate particle dispersion sol as claimed in claim 11 having an absorbance (ABS) of 2.0 or less exhibited when the  $\text{Al}_2\text{O}_3$  has a concentration of 20% by weight.

14/13. A coating liquid for forming an ink receptive layer, comprising:  
alumina hydrate particles and a binder, wherein said particles and binder are dispersed in one of water or an organic solvent,

wherein the alumina hydrate particles have a composition represented by the general formula:



$$2 \times 10^{-4} \leq 10^{-4} \leq x \leq 25 \times 10^{-4}$$

$$0.1 \times 10^{-4} \leq y \leq 20 \times 10^{-4}$$

$$0.6 \leq z \leq 2.5$$

wherein M represents an alkali metal; when the alkali metal is in the form of  $\text{M}_2\text{O}$ , x is the number of moles thereof per mol of  $\text{Al}_2\text{O}_3$ ; when ammonia is in the form of  $(\text{NH}_4)_2\text{O}$ , y is the number of moles thereof per mol of  $\text{Al}_2\text{O}_3$ ; and z is the number of moles of hydration water ( $\text{H}_2\text{O}$ ) per mol of  $\text{Al}_2\text{O}_3$ ,

said alumina hydrate particles having:

an average particle diameter of 0.02 to 0.2  $\mu\text{m}$ ,

a total pore volume of 0.5 to 1.5 ml/g, and

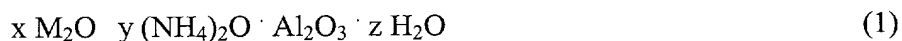
a volume of pores whose diameter is from 15 to 30 nm ranging from 0.3 to 1.0 ml/g.

15/4.

A recording sheet with ink receptive layer, comprising a substrate sheet having an ink receptive layer formed thereon from a coating liquid comprising:

alumina hydrate particles and a binder, wherein said particles and binder are dispersed in one of water or an organic solvent,

wherein the alumina hydrate particles have a composition represented by the general formula:



$$2 \times 10^{-4} \leq 10^{-4} \leq x \leq 25 \times 10^{-4}$$

$$0.1 \times 10^{-4} \leq y \leq 20 \times 10^{-4}$$

$$0.6 \leq z \leq 2.5$$

wherein M represents an alkali metal; when the alkali metal is in the form of  $M_2O$ , x is the number of moles thereof per mol of  $Al_2O_3$ ; when ammonia is in the form of  $(NH_4)_2O$ , y is the number of moles thereof per mol of  $Al_2O_3$ ; and z is the number of moles of hydration water ( $H_2O$ ) per mol of  $Al_2O_3$ ,

said alumina hydrate particles having:

an average particle diameter of 0.02 to 0.2  $\mu m$ ,

a total pore volume of 0.5 to 1.5 ml/g, and

a volume of pores whose diameter is from 15 to 30 nm ranging from 0.3 to 1.0

ml/g.

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**IN THE ABSTRACT:**

Please replace the section heading beginning at page 42, line 1 with the following section heading:

**ABSTRACT OF THE DISCLOSURE**

**REMARKS**


The specification and claims have been amended to place the application in conformance with standard United States patent practice.

Attached hereto is a marked-up version of the changes made to the specification by the current amendment. The attachment is captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE".

Examination and allowance of pending claims 7-14 are respectfully requested.

Respectfully submitted,

WEBB ZIESENHEIM LOGSDON  
ORKIN & HANSON, P.C.

By   
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**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**In the specification:**

**Section heading beginning at page 1, line 7 has been amended as follows:**

[TECHNICAL FIELD] BACKGROUND OF THE INVENTION

1. Field of the Invention

**Section heading beginning at page 1, line 22 has been amended as follows:**

[BACKGROUND ART] 2. Description of the Prior Art

**Paragraph beginning at page 4, line 22 has been amended as follows:**

The present invention has been made with a view toward solving the above problems of the prior art. [Therefore, it is an object of] In overcoming these problems, the present invention [to provide] provides alumina hydrate particles [having] and a process for producing same wherein the particles have a large pore volume and [having] have a pore diameter which falls in a specified range, and [to provide] , in addition, provides a highly transparent alumina hydrate particle dispersion sol which, even if in a high concentration, exhibits a low viscosity.

**Paragraph beginning at page 5, line 5 has been amended as follows:**

[It is another object of the] The present invention [to provide] further provides a coating liquid for forming an ink receptive layer wherein the above alumina hydrate particles are contained, and [to provide] provides a substrate with an ink receptive layer formed with the use of the coating liquid.

**Section heading beginning at page 5, line 11 has been amended as follows:**

[DISCLOSURE] SUMMARY OF THE INVENTION

**Section heading beginning at page 7, line 12 has been amended as follows:**

[BEST MODE FOR CARRYING OUT] DETAILED DESCRIPTION OF THE INVENTION

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**In the abstract:**

**The section heading beginning at page 42 line 1 has been amended as follows:**

**ABSTRACT OF THE DISCLOSURE**

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DESCRIPTION

NOVEL ALUMINA HYDRATE PARTICLE, ALUMINA HYDRATE  
PARTICLE DISPERSION SOL, COATING LIQUID FOR  
FORMING INK RECEPTIVE LAYER AND SUBSTRATE WITH INK  
5 RECEPTIVE LAYER

TECHNICAL FIELD

The present invention relates to alumina hydrate  
particles, an alumina hydrate particle dispersion sol, and  
10 a coating liquid for forming an ink receptive layer wherein  
the alumina hydrate particles are contained. More  
particularly, the present invention relates to highly  
transparent alumina hydrate particles which contain  
alkali metal oxide and ammonia components in extremely  
15 minute amounts and which, when dispersed in water, exhibits  
a low viscosity, and further relates to a sol wherein the  
alumina hydrate particles are dispersed, to a coating liquid  
for forming an ink receptive layer wherein the alumina  
hydrate particles are contained, and to a substrate with  
20 ink receptive layer obtained from the coating liquid.

BACKGROUND ART

Fine particles of a metal oxide such as silica, alumina  
or alumina hydrate, fine particles of a metal hydroxide and  
25 sols obtained by dispersing these in solvents have been used

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in various fields. For example, there can be mentioned uses in a catalyst, a catalyst support, a material for film formation, a filler incorporated in a resin, various binders, a slip improver, a lubricant, a thickener, cosmetic ingredients, etc.

Recently, there is an increasing expectation for the use of alumina or alumina hydrate particles for formation of a receptive layer on a printing recording medium. For example, it is described in Japanese Patent Publication No. 3(1991)-24906 that a recording medium having a receptive layer wherein a cationic hydrated aluminum oxide is contained is highly suitable for printing with a water soluble dye ink.

It is further described in Japanese Patent Publication No. 4(1992)-115984 that a recording sheet comprising a layer of pseudoboehmite alumina and, superimposed thereon, a layer of porous silica is highly transparent and exhibits high ink absorbency.

It is still further described in Japanese Patent Laid-open Publication No. 6(1994)-55829 that a recording sheet a layer of porous silica particles having an average particle diameter of 2 to 50  $\mu\text{m}$ , an average pore diameter of 8 to 50 nm and a pore volume of 0.8 to 2.5 cc/g and, superimposed thereon, a porous layer of pseudoboehmite

obtained by drying alumina sol exhibits high ink absorbency and is excellent in pigment stability.

On the other hand, the inventors proposed in Japanese Patent Application No. 10(1998)-206284 a recording sheet  
5 with ink receptive layer prepared using a coating liquid for forming an ink receptive layer which contained oxide particles of positive  $\zeta$ -potential carrying on their surfaces a cationic hydrated metal compound, in particular, containing  $Al^{3+}$  as a metal cation. The recording sheet was  
10 described as being free from blotting, enabling clear printing, and being excellent in water resistance, weather resistance, fading tendency, etc.

However, when conventional alumina particles of small pore diameter or small pore volume are employed, although  
15 pigment stability is excellent, the ink absorption speed is low and also the ink absorption capacity is small, so that blotting and unclearness have been experienced.

Moreover, the average pore diameter of alumina and alumina hydrate particles is generally in the range of about  
20 5 to 15 nm, and it is difficult to obtain those of greater pore diameter. Even if those were obtained, the pore volume would be unfavorably small, and there would occur the problem of economic inefficiency caused by, for example, the need for post-treatment and special technique.

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Further, with respect to the conventional alumina sol or alumina hydrate particle dispersion sol, the viscosity is high and the particles are likely to aggregate together, so that various problems have been posed. For example, it is difficult to prepare a high-concentration sol wherein the concentration of  $\text{Al}_2\text{O}_3$  is about 8% by weight or greater, thereby necessitating transportation of a low-concentration sol. This would increase transportation cost. In the aforementioned uses, the preparation of a low-concentration sol only would, for example, disenable forming a thick coating because of the low concentration at the time of coating formation. For increasing the coating thickness, it would unfavorably be needed to repeat application and drying of a coating liquid.

Still further, even if a high-concentration sol is prepared from conventional alumina or alumina hydrate particles, there have been problems such that the transparency of the sol is poor and that the viscosity of the sol is extremely high.

In particular, it has been difficult to obtain a sol of high transparency and low viscosity from porous alumina.

The present invention has been made with a view toward solving the above problems of the prior art. Therefore, it is an object of the present invention to provide alumina hydrate particles having a large pore volume and having a

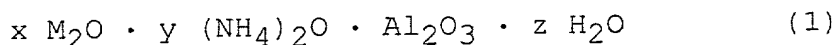
pore diameter which falls in a specified range, and to provide a highly transparent alumina hydrate particle dispersion sol which, even if in a high concentration, exhibits a low viscosity.

5 It is another object of the present invention to provide a coating liquid for forming an ink receptive layer wherein the above alumina hydrate particles are contained, and to provide a substrate with ink receptive layer formed with the use of the coating liquid.

10

#### DISCLOSURE OF THE INVENTION

The alumina hydrate particles of the present invention have a composition represented by the general formula:



15

$$2 \times 10^{-4} \leq x \leq 25 \times 10^{-4}$$

$$0.1 \times 10^{-4} \leq y \leq 20 \times 10^{-4}$$

$$0.6 \leq z \leq 2.5$$

wherein M represents an alkali metal; when the alkali metal is in the form of  $\text{M}_2\text{O}$ , x is the number of moles thereof per mol of  $\text{Al}_2\text{O}_3$ ; when ammonia is in the form of  $(\text{NH}_4)_2\text{O}$ , y is the number of moles thereof per mol of  $\text{Al}_2\text{O}_3$ ; and z is the number of moles of hydration water ( $\text{H}_2\text{O}$ ) per mol of  $\text{Al}_2\text{O}_3$ ,

20

the alumina hydrate particles having:

25

an average particle diameter of 0.02 to 0.2  $\mu\text{m}$ ,

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a total pore volume of 0.5 to 1.5 ml/g, and  
a volume of pores whose diameter is from 15 to 30 nm  
ranging from 0.3 to 1.0 ml/g.

The process for producing alumina hydrate particles  
5 according to the present invention comprises the steps of:

neutralizing an aqueous solution of alkali metal  
aluminate or an aqueous solution of aluminum salt to thereby  
form an alumina hydrogel;

separating the alumina hydrogel by filtration, and  
10 washing the separated alumina hydrogel with water and/or  
aqueous ammonia;

adjusting the pH value of the washed alumina hydrogel  
so as to fall within the range of 9 to 12, and heating the  
alumina hydrogel at 50 to 105°C to thereby effect aging of  
15 the alumina hydrogel;

adding an acid to the alumina hydrogel so that the  
alumina hydrogel is deflocculated into an alumina hydrosol;  
and

drying the alumina hydrosol.

20 The alumina hydrate particle dispersion sol of the  
present invention comprises a dispersion of the above alumina  
hydrate particles in water. This alumina hydrate particle  
dispersion sol preferably has a viscosity of 50 to 2000 cP  
exhibited when the  $\text{Al}_2\text{O}_3$  has a concentration of 20% by weight.

25 Further, this alumina hydrate particle dispersion sol

preferably has an absorbance (ABS) of 0.6 or less exhibited when the  $\text{Al}_2\text{O}_3$  has a concentration of 20% by weight.

The coating liquid for forming an ink receptive layer according to the present invention comprises:

- 5       the above alumina hydrate particles, and a binder, both dispersed in water and/or an organic solvent.

The substrate with ink receptive layer according to the present invention comprises a substrate sheet having an ink receptive layer formed thereon from the above coating liquid for forming an ink receptive layer.

10

#### BEST MODE FOR CARRYING OUT THE INVENTION

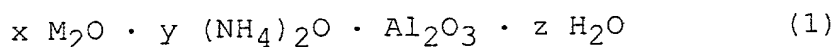
The alumina hydrate particles, alumina hydrate particle dispersion sol and coating liquid for forming an ink receptive layer according to the present invention will be described in detail below.

15

[Alumina hydrate]

The alumina hydrate of the present invention is characterized by being represented by the following general formula (1), and contains an alkali metal and ammonia in a specified ratio.

20



wherein M represents an alkali metal; when the alkali metal is in the form of  $\text{M}_2\text{O}$ , x is the number of moles thereof per mol of  $\text{Al}_2\text{O}_3$ ; when ammonia is in the form of  $(\text{NH}_4)_2\text{O}$ ,

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y is the number of moles thereof per mol of  $\text{Al}_2\text{O}_3$ ; and z is the number of moles of hydration water ( $\text{H}_2\text{O}$ ) per mol of  $\text{Al}_2\text{O}_3$ .

When the alkali metal of alumina hydrate particles is  
5 in the form of  $\text{M}_2\text{O}$ , the number of moles thereof (x) is in the range of  $2 \times 10^{-4}$  to  $25 \times 10^{-4}$  mol, preferably  $3 \times 10^{-4}$  to  $20 \times 10^{-4}$  mol, per mol of  $\text{Al}_2\text{O}_3$ . When the amount of alkali metal oxide  $\text{M}_2\text{O}$  is less than  $2 \times 10^{-4}$  mol, the recording sheet with ink receptive layer formed using the alumina  
10 hydrate particles may suffer from discoloration when printing is effected thereon. It is presumed that the reason for discoloration will be that, when the amount of alkali metal oxide is less than  $2 \times 10^{-4}$  mol, the surface activity of alumina hydrate is so high that contained dye or other  
15 organic matter will be affected. On the other hand, when the amount of alkali metal oxide exceeds  $25 \times 10^{-4}$  mol, the stability of sol wherein the alumina hydrate particles are dispersed may be lowered, or the viscosity thereof may be increased, so that it may be difficult to obtain a  
20 high-concentration sol.

When the ammonia of alumina hydrate particles is in the form of  $(\text{NH}_4)_2\text{O}$ , the number of moles thereof (y) is in the range of  $0.1 \times 10^{-4}$  to  $20 \times 10^{-4}$  mol per mol of  $\text{Al}_2\text{O}_3$ . When the amount of  $(\text{NH}_4)_2\text{O}$  is less than  $0.1 \times 10^{-4}$  mol, the  
25 recording sheet with ink receptive layer formed using the

alumina hydrate particles, when printing is effected thereon, may suffer from decoloration of printed color. On the other hand, when the amount of  $(\text{NH}_4)_2\text{O}$  exceeds  $20 \times 10^{-4}$  mol, the stability of sol wherein the alumina hydrate particles are dispersed may be lowered, or the viscosity thereof may be increased, so that it may be difficult to obtain a high-concentration sol.

The number of moles of hydration water ( $\text{H}_2\text{O}$ ) per mol of  $\text{Al}_2\text{O}_3$ ,  $z$ , is in the range of 0.6 to 2.5 mol.

10 When the amount of hydration water is less than 0.6 mol, the dispersibility of alumina hydrate particles may be lowered, and the amount of electric charge on alumina hydrate particles tends to decrease so as to lower ink absorbency. On the other hand, when the amount of hydration  
15 water exceeds 2.5 mol, the pore volume of alumina hydrate particles tends to be small so as to lower ink absorbency.

Herein, the terminology "hydration water" refers to water remaining even after drying of alumina hydrate particles at  $100^\circ\text{C}$  for 2 hr. The amount of hydration water  
20 is determined by drying a sample at  $100^\circ\text{C}$  for 2 hr, heating the sample up to  $600^\circ\text{C}$  in a stream of  $\text{N}_2$  to thereby evolve a gas and then measuring the water content of the gas according to the Karl Fischer method.

The average particle diameter of these alumina hydrate particles is in the range of 0.02 to 0.2  $\mu\text{m}$ , preferably 0.03 to 0.15  $\mu\text{m}$ .

When the average particle diameter of alumina hydrate particles is less than 0.02  $\mu\text{m}$ , the alumina hydrate particle dispersion sol has a high viscosity, and accordingly the coating liquid for forming an ink receptive layer prepared therefrom has a high viscosity. Thus, the coating liquid may have poor applicability. On the other hand, when the average particle diameter of alumina hydrate particles exceeds 0.2  $\mu\text{m}$ , the alumina hydrate particle dispersion sol may have poor transparency. Thus, the obtained ink receptive layer may have poor transparency and poor printed image clearness.

The average particle diameter of alumina hydrate particles has been measured by means of particle size distribution meter (model CAPA-700, manufactured by Horiba Seisakusho Co., Ltd.).

The total pore volume of these alumina hydrate particles is in the range of 0.5 to 1.5 ml/g, preferably 0.6 to 1.4 ml/g. When the total pore volume is less than 0.5 ml/g, the ink receptive layer obtained from the alumina hydrate particles may exhibit poor ink absorbency to thereby disenable clear printing. On the other hand, when the total

pore volume exceeds 1.5 ml/g, ink blotting may be likely to occur.

With respect to these alumina hydrate particles, the volume of pores whose diameter is from 15 to 30 nm is in the range of 0.25 to 1.0 ml/g, preferably 0.3 to 0.8 ml/g. When the volume of pores whose diameter is from 15 to 30 nm is less than 0.25 ml/g, the ink receptive layer obtained from the alumina hydrate particles may exhibit poor ink absorbency and unfavorably low ink absorption speed to thereby cause blotting and disenable clear printing. On the other hand, when the volume of pores whose diameter is from 15 to 30 nm exceeds 1.0 ml/g, the water resistance tends to be poor.

The total pore volume of alumina hydrate particles has been determined by measuring the volume of pores whose diameter is 600 Å or greater by means of mercury penetration porosimeter (model 2000, manufactured by Amco Inc.), measuring the volume of pores whose diameter is less than 600 Å according to the N<sub>2</sub> adsorption method and summing these two pore volume measurements. The volume of pores whose diameter is from 15 to 30 nm has been determined from that obtained in the above measuring of total pore volume.

These alumina hydrate particles are produced by, for example, the following process.

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First, an aqueous solution of alkali metal aluminate or an aqueous solution of aluminum salt is neutralized to thereby form an alumina hydrogel.

The aqueous solution of alkali metal aluminate can be  
5 an aqueous solution of a water soluble salt such as sodium aluminate or potassium aluminate. An aqueous solution of sodium aluminate is especially preferably used.

The aqueous solution of aluminum salt can be, for example, an aqueous solution of aluminum sulfate or an  
10 aqueous solution of aluminum chloride. An aqueous solution of aluminum sulfate is preferred.

For example, the alumina hydrogel can be prepared by neutralizing an aqueous solution of alkali metal aluminate or an aqueous solution of aluminum salt, optionally in the  
15 presence of an alkali such as an alkali metal hydroxide and/or aqueous ammonia, or an acid such as a mineral acid or an organic acid. Also, the alumina hydrogel can be prepared by neutralizing an aqueous solution of alkali metal aluminate with an acidic compound such as a mineral acid or an organic  
20 acid. Further, the alumina hydrogel can be prepared by neutralizing an aqueous solution of aluminum salt with an alkali metal hydroxide and/or aqueous ammonia.

The aqueous solution of alkali metal hydroxide can be an aqueous solution of, for example, any of lithium hydroxide,  
25 sodium hydroxide, potassium hydroxide and strontium

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hydroxide. Of these, an aqueous solution of sodium hydroxide or potassium hydroxide is preferred. As an ammonia component, use can be made of urea which evolves ammonia when decomposed.

5       The mineral acid can be, for example, sulfuric acid, hydrochloric acid or nitric acid. The organic acid can be, for example, acetic acid, oxalic acid or citric acid.

10       A crystal growth inhibitor may optionally be added to the aqueous solution. A carboxylic acid such as gluconic acid, aspartic acid or adipic acid, or a carboxylic acid salt such as a gluconate, an aspartate or an adipate is preferably used as the crystal growth inhibitor.

15       The concentration of each of the above aqueous solutions, although not particularly limited as long as the alumina hydrogel can be formed, is preferably such that the concentration of formed  $\text{Al}_2\text{O}_3$  is in the range of 1 to 5% by weight.

It is preferred that the pH value of prepared alumina hydrogel be in the range of about 9 to 12.

20       Further, it is preferred that, at the time of preparation, the liquid temperature of alumina hydrogel be in the range of 10 to 50°C.

25       The thus prepared alumina hydrogel is separated by filtration, and washed with water and/or aqueous ammonia to thereby remove salts. This washing is performed so that

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the amount of alkali metal contained in alumina hydrate particles is in the range of  $2 \times 10^{-4}$  to  $20 \times 10^{-4}$  mol, in terms of oxide, per mol of  $\text{Al}_2\text{O}_3$ .

The water content of washed alumina hydrogel is regulated so that the concentration in terms of  $\text{Al}_2\text{O}_3$  is in the range of about 1 to 7% by weight. The pH value thereof is adjusted so as to fall within the range of 9 to 12 by optionally adding aqueous ammonia. Subsequently, the alumina hydrogel is heated at 50 to  $105^\circ\text{C}$ , preferably 80 to  $105^\circ\text{C}$ , for 10 to 100 hr to thereby effect aging of the alumina hydrogel.

Contained ammonia is preferably evaporated off as completely as possible during or after the aging of alumina hydrogel. Thus, the pressure may optionally be reduced to vacuum after the completion of aging to thereby remove ammonia. It is preferred that the removal of ammonia be effected until the ion conductivity of alumina hydrogel slurry falls within the range of 10 to  $1000 \mu\text{S}/\text{cm}$ . When the ion conductivity is in this range, the content of ammonia, in the form of  $(\text{NH}_4)_2\text{O}$ , in finally obtained particles can be in the range of  $0.1 \times 10^{-4}$  to  $20 \times 10^{-4}$  mol per mol of  $\text{Al}_2\text{O}_3$ .

An alumina hydrosol can be obtained by adding an acid to the washed alumina hydrogel to thereby deflocculate the same. The added acid can be a mineral acid such as

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hydrochloric acid or nitric acid, or an organic acid such as acetic acid, as aforementioned.

The amount of added acid is preferably to be minimized as long as the deflocculation can be accomplished. The amount of acid is preferably about 0.2 mol or less per mol of  $\text{Al}_2\text{O}_3$ .

The alumina hydrosol obtained by the deflocculation is dried in hot air so as to obtain the alumina hydrate particles of the present invention. The alumina hydrate particle dispersion sol of the present invention can be obtained by dispersing the obtained alumina hydrate particles in water.

Although the drying method is not particularly limited as long as it is not detrimental to the dispersibility of obtained alumina hydrate particles, spray drying and similar drying methods are preferred from the viewpoint that the probability of adverse effect thereof on the dispersibility is low.

In the spray drying, it is preferred that the temperature of hot air fed into spray drying zone be in the range of 150 to 400°C and that the temperature of gas discharged from the spray drying zone be in the range of 60 to 150°C.

When the temperature of hot air fed into spray drying zone is lower than 150°C, it may occur that the content of

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ammonia, in the form of  $(\text{NH}_4)_2\text{O}$ , in alumina hydrate particles cannot be  $20 \times 10^{-4}$  mol or less per mol of  $\text{Al}_2\text{O}_3$  to thereby disenable obtaining the alumina hydrate particles and alumina hydrate particle dispersion sol of high concentration, low viscosity and high transparency according to the present invention. On the other hand, when the above temperature exceeds  $400^\circ\text{C}$ , although the content of ammonia, in the form of  $(\text{NH}_4)_2\text{O}$ , can be  $0.1 \times 10^{-4}$  mol or less per mol of  $\text{Al}_2\text{O}_3$ , the dispersibility thereof in a solvent (water) would be lowered to thereby cause obtaining a stable homogeneous sol or coating liquid to be difficult. Further, an alteration of printed color may be caused.

[Alumina hydrate particle dispersion sol]

The alumina hydrate particle dispersion sol of the present invention is a dispersion of the above alumina hydrate particles in water.

The viscosity of this alumina hydrate particle dispersion sol, exhibited when the concentration in terms of  $\text{Al}_2\text{O}_3$  is 20% by weight, is preferably in the range of 50 to 2000 cP, still preferably 100 to 500 cP.

When the above viscosity is lower than 50 cP, the viscosity of the coating liquid such as the coating liquid for forming an ink receptive layer may be so low that it is difficult to form a thick coating film by one-time application. On the other hand, when the above viscosity

of alumina hydrate particle dispersion sol exceeds 2000 cP, the viscosity of the coating liquid may be so high that handling of the coating liquid is difficult. Diluting this coating liquid in order to lower the viscosity thereof may  
5 cause formation of a thick coating film by one-time application to be difficult.

The absorbance (ABS) of alumina hydrate particle dispersion sol prepared so that the concentration in terms of  $\text{Al}_2\text{O}_3$  is 20% by weight is preferably 2.0 or less, still  
10 preferably 1.5 or less. When the absorbance exceeds 2.0, the transparency of the coating film obtained from the alumina hydrate particles may be unsatisfactory.

The viscosity has been measured by the use of viscometer (model BM, manufactured by Tokimec, Inc.). With respect  
15 to the absorbance, that at a wavelength of 550 nm was measured by the use of spectrophotometer (model U-2000, manufactured by Hitachi, Ltd.).

With respect to the alumina hydrate particle dispersion sol of the present invention, because the above alumina  
20 hydrate particles of specified composition are dispersed therein, the concentration in terms of  $\text{Al}_2\text{O}_3$  can be increased up to about 40% by weight. When the concentration in terms of  $\text{Al}_2\text{O}_3$  exceeds 40% by weight, the viscosity of the coating liquid may be so high that the coating liquid cannot be handled

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and that it is difficult to form a coating film of uniform thickness.

[Coating liquid for forming ink receptive layer]

The coating liquid for forming an ink receptive layer  
5 according to the present invention comprises the above  
alumina hydrate particles and a binder, both dispersed in  
water and/or an organic solvent.

#### Binder

Mainly, hydrophilic polymers are used as a binder in  
10 the coating liquid for forming an ink receptive layer  
according to the present invention. Examples of such  
hydrophilic polymers include polyvinyl alcohol, modified  
polyvinyl alcohol and polyvinylpyrrolidone. These can be  
modified before use. Also, hydrophobic polymers can be used  
15 as the binder.

The amount of binder added, although varied depending  
on the type of binder, is preferably in the range of 5 to  
60% by weight, still preferably 10 to 40% by weight, based  
on the weight of alumina hydrate particles.

20 When the amount of binder is less than 5% by weight,  
the adherence between the ink receptive layer and a substrate  
sheet may be so poor that the ink receptive layer is easily  
peeled off. Also, the strength of the ink receptive layer  
may be poor. On the other hand, when the amount of binder  
25 exceeds 60% by weight, it may occur that the amount of ink

reception is unfavorably reduced and that the water resistance is unsatisfactory.

The coating liquid for forming an ink receptive layer according to the present invention may contain, in addition  
5 to the above oxide particles and binder, an antioxidant, organic polymers such as celluloses, bio-fibers, an inorganic polymer, inorganic fine particles, etc. in order to enhance the adherence between ink receptive layer and substrate sheet, to increase the strength and weather  
10 resistance of ink receptive layer, or to regulate the pore structure of ink receptive layer.

Water and/or an organic solvent is used as a dispersion medium in the coating liquid for forming an ink receptive layer according to the present invention. The organic  
15 solvent can be, for example, isopropyl alcohol, ethanol or butanol.

The coating liquid for forming an ink receptive layer can be prepared by dispersing the above alumina hydrate particles in water and mixing the above components into the  
20 dispersion.

The concentration of alumina hydrate particles in the coating liquid, although appropriately selected depending on the application method, is preferably in the range of 2 to 40% by weight, still preferably 5 to 30% by weight.

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When the concentration is lower than 2% by weight, the concentration of the coating liquid for coating film formation cannot be high to thereby disenable obtaining a thick coating film. On the other hand, when the

5 concentration of alumina hydrate particles exceeds 40% by weight, the viscosity of the coating liquid may be so high that the coating liquid cannot be handled, or drying irregularity occurs, with the result that formation of a uniform coating film is difficult.

10 [Method of forming ink receptive layer and ink receptive layer]

Customary methods can be employed for forming the ink receptive layer on a substrate sheet. Preferable methods can be employed depending on the type of substrate.

15 For example, the ink receptive layer can be formed by coating a substrate sheet with the above coating liquid for forming an ink receptive layer by the spray method, roll coater method, blade coater method, bar coater method, curtain coater method or the like, and thereafter drying

20 the coating liquid.

The substrate may be pretreated with a primer before coating operation.

The substrate sheet for use in the present invention is not particularly limited, and can be, for example, any

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of a film sheet of a resin such as PET or polyvinyl chloride, various types of papers, a copper plate and a cloth.

In the thus formed ink receptive layer, it is preferred that the total pore volume thereof be in the range of 0.5 to 1.5 ml/g, especially 0.7 to 1.3 ml/g.

When the total pore volume of ink receptive layer is less than 0.5 ml/g, the volume of ink absorbed may be so small that blotting occurs to thereby disenable obtaining clear high-precision images. On the other hand, when the total pore volume of ink receptive layer is greater than 1.5 ml/g, dye fixability may be deteriorated, and the strength of ink receptive layer may be unfavorably low.

The thickness of ink receptive layer formed on the substrate sheet, although can appropriately be selected depending on the thickness of sheet, the usage of printed matter, the type of printing ink, etc., is preferably in the range of 5 to 100  $\mu\text{m}$ . When the thickness of ink receptive layer is less than 5  $\mu\text{m}$ , the volume of ink absorbed may be so small that blotting occurs, or that, when the amount of ink used is reduced, color is not clear. The ink receptive layer whose thickness is greater than 100  $\mu\text{m}$  is difficult to obtain the same by one-time application. Performing a plurality of applications in order to form the ink receptive layer having thickness of greater than 100  $\mu\text{m}$  is not only

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economically disadvantageous but also, at the time of drying after application, may cause cracking or peeling.

#### EFFECT OF THE INVENTION

5       The alumina hydrate particles (powder) of the present invention contain specified amounts of alkali metal oxide and ammonia. Accordingly, the surface activity of alumina hydrate is so low that the deterioration of an organic substance such as a dye by the surface activity of alumina hydrate is inhibited. Therefore, the recording sheet with ink receptive layer formed using these alumina hydrate particles can be free from discoloration at the time of printing. These alumina hydrate particles, even if dispersed in high concentration, can be free from sol stability lowering or viscosity increase, so that a thick coating film can be formed therefrom.

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These alumina hydrate particles (powder) have a large pore diameter and an increased pore volume, so that the use thereof in the formation of an ink receptive layer realizes an ink receptive layer which is excellent in pigment stability, exhibits a high ink absorption speed and has a large ink absorption capacity and which is free from blotting.

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#### EXAMPLES

The present invention will be further illustrated below with reference to the following Examples, which in no way limit the scope of the invention.

Example 1

5        Preparation of alumina hydrate particle

While agitating 12.7 kg of an aqueous solution of sodium aluminate (concentration in terms of  $\text{Al}_2\text{O}_3$ : 3% by weight), 7.3 g of a 26% by weight aqueous solution of sodium gluconate was added thereto, and further 25 kg of an aqueous solution of aluminum sulfate (concentration in terms of  $\text{Al}_2\text{O}_3$ : 1.5% by weight) was added over a period of 12 min. Thus, an alumina hydrogel was obtained. At the time of preparation of the alumina hydrogel, the liquid temperature of alumina hydrogel is 30°C and pH of the obtained alumina hydrogel is 10.2.

10        Thereafter, the agitation was discontinued, and the alumina hydrogel was aged at 30°C for 90 min.

The formed alumina hydrogel was separated by filtration, and washed with 1.5% aqueous ammonia. The amounts of alkali and sulfate radicals remaining in alumina were 0.022% by weight in terms of  $\text{Na}_2\text{O}$  and 0.062% by weight in terms of  $\text{SO}_4$  (both based on dry alumina powder), respectively.

20        Water was added to the washed alumina hydrogel so as to adjust the concentration in terms of  $\text{Al}_2\text{O}_3$  to 5.0% by weight. Subsequently, 15% aqueous ammonia was added so as to adjust the pH value to 11.2, and, under slow agitation,

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aging of alumina hydrogel was performed at 95°C for 80 hr. During the aging, the pH value was adjusted to 11.2 by adding 15% aqueous ammonia.

The removal of ammonia was performed for about 20 hr until the conductivity of alumina hydrogel slurry became 100  $\mu\text{S}/\text{cm}$  by exhausting evaporated steam and ammonia gas while maintaining the temperature at 100 to 105°C.

After the removal of ammonia, the temperature was lowered to 95°C. Acetic acid was added in an amount of 5.5% by weight based on the weight of  $\text{Al}_2\text{O}_3$ , agitated for 3 hr, and cooled to 35°C. Pure water was added, thereby obtaining an alumina hydrosol having a concentration in terms of  $\text{Al}_2\text{O}_3$  of 5.0% by weight.

The thus obtained alumina hydrosol was charged into a spray dryer, and spray drying was performed while controlling the temperature of hot air fed into spray drying zone at 250°C and controlling the temperature of gas discharged from the spray drying zone at  $100 \pm 10^\circ\text{C}$ . Thus, powder of alumina hydrate particles (A) was obtained.

With respect to the obtained alumina hydrate particles (A), the alkali metal content, ammonia content, average particle diameter and total pore volume were measured.

The results are listed in Table 1.

Preparation of water dispersion sol

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Alumina hydrate particles (A) were dispersed in water, thereby obtaining a water dispersion sol having an  $\text{Al}_2\text{O}_3$  concentration of 20% by weight. The viscosity thereof was measured. Further, a water dispersion was prepared by  
5 dispersing alumina hydrate particles (A) so that the concentration in terms of  $\text{Al}_2\text{O}_3$  became 20% by weight, and the absorbance thereof was measured.

The results are also listed in Table 1.

Preparation of coating liquid for forming ink receptive  
10 layer

The above obtained alumina hydrate particles (A) were dispersed in water so that the solid concentration became 15% by weight. 100 parts by weight of this dispersion and 37.5 parts by weight of a 10% by weight aqueous solution  
15 of polyvinyl alcohol were mixed together, thereby obtaining a coating liquid.

Preparation of recording sheet

The obtained coating liquid was applied onto a PET film by means of a bar coater, dried, and heated at  $140^\circ\text{C}$ . Thus,  
20 a recording sheet was obtained. The thickness of ink receptive layer was 30  $\mu\text{m}$ .

The following printing was performed on the obtained recording sheet, and evaluated.

The results are also listed in Table 1.

25 Printing

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Pattern W of 2 cm square was printed all over on the obtained recording sheet by means of ink jet printer (Masterjet, manufactured by Graphtec) with the use of genuine dye inks. Magenta, black, cyan and yellow colors were used, and printing was effected while varying densities by changing the output. The following evaluation was conducted to obtainable printed sheet.

[Density]

The density was measured by means of color reflectometer (KRD-2200, manufactured by Nippon Denshoku Kogyo Co., Ltd.). When the density is 1.2 or higher, use can be made without any particular problem.

[Blotting]

The configuration of each printed dot was observed through a microscope, and evaluated on the following criteria:

Excellent: completely circular, and no blotting observed,

Good : circular, but slight blotting observed, and

Poor : circular, but clear blotting observed.

[Drying speed]

With respect to two overlapped dots with different colors, the mixing of color was observed through a microscope, and evaluated on the following criteria:

Excellent: no color mixing observed,

10070110-022802

Good : slight color mixing observed, and

Poor : clear color mixing observed.

[Water resistance]

Printed pieces were immersed in water, and the leaching  
5 of pigment and dye therefrom was observed. Evaluation was  
made on the following criteria:

Excellent: no blotting observed,

Good : slight blotting observed,

Poor : clear blotting observed, and

10 Very poor: leaching of pigment or dye observed.

#### Example 2

Alumina hydrate particles (B) were prepared in the same  
manner as in Example 1 except that, in the washing step of  
Example 1, washing was performed with 0.5% aqueous ammonia  
15 in place of 1.5% aqueous ammonia.

After this ammonia washing, the amounts of alkali and  
sulfate radicals remaining in alumina hydrate particles (B)  
were 0.12% by weight in terms of  $\text{Na}_2\text{O}$  (on dry basis) and  
0.28% by weight in terms of  $\text{SO}_4$  (on dry basis), respectively,  
20 based on the weight of  $\text{Al}_2\text{O}_3$ .

After the removal of ammonia, the conductivity of  
alumina hydrogel slurry was  $250 \mu\text{S}/\text{cm}$ .

With respect to the obtained alumina hydrate particles  
(B), the alkali metal content, ammonia content, average  
25 particle diameter and total pore volume were measured.

The results are listed in Table 1.

Preparation of water dispersion sol

Alumina hydrate particles (B) were dispersed in water, thereby obtaining a water dispersion sol having an  $\text{Al}_2\text{O}_3$  concentration of 20% by weight. The viscosity thereof was measured. Further, a water dispersion was prepared by dispersing alumina hydrate particles (B) so that the concentration in terms of  $\text{Al}_2\text{O}_3$  became 20% by weight, and the absorbance thereof was measured.

10 The results are also listed in Table 1.

Preparation of coating liquid for forming ink receptive layer

The above obtained alumina hydrate particles (B) were dispersed in water so that the solid concentration became 15% by weight. 100 parts by weight of this dispersion and 37.5 parts by weight of a 10% by weight aqueous solution of polyvinyl alcohol were mixed together, thereby obtaining a coating liquid.

Preparation of recording sheet

20 The obtained coating liquid was applied onto a PET film by means of a bar coater, dried, and heated at  $140^\circ\text{C}$ . Thus, a recording sheet was obtained. The thickness of ink receptive layer was  $30\ \mu\text{m}$ .

In the same manner as in Example 1, printing was performed on the obtained recording sheet and evaluated.

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The results are also listed in Table 1.

### Example 3

Powder of alumina hydrate particles (C) was prepared in the same manner as in Example 1 except that, in the ammonia removal step of Example 1, the removal of ammonia was performed for about 80 hr until the conductivity of alumina hydrogel slurry became 50  $\mu\text{S}/\text{cm}$ .

With respect to the obtained alumina hydrate particles (C), the alkali metal content, ammonia content, average particle diameter and total pore volume were measured.

The results are listed in Table 1.

### Preparation of water dispersion sol

Alumina hydrate particles (C) were dispersed in water, thereby obtaining a water dispersion sol having an  $\text{Al}_2\text{O}_3$  concentration of 20% by weight. The viscosity thereof was measured. Further, a water dispersion was prepared by dispersing alumina hydrate particles (C) so that the concentration in terms of  $\text{Al}_2\text{O}_3$  became 20% by weight, and the absorbance thereof was measured.

The results are also listed in Table 1.

### Preparation of coating liquid for forming ink receptive layer

The above obtained alumina hydrate particles (C) were dispersed in water so that the solid concentration became 15% by weight. 100 parts by weight of this dispersion and



37.5 parts by weight of a 10% by weight aqueous solution of polyvinyl alcohol were mixed together, thereby obtaining a coating liquid.

#### Preparation of recording sheet

5        The obtained coating liquid was applied onto a PET film by means of a bar coater, dried, and heated at 140°C. Thus, a recording sheet was obtained. The thickness of ink receptive layer was 30  $\mu\text{m}$ .

10       In the same manner as in Example 1, printing was performed on the obtained recording sheet and evaluated.

The results are also listed in Table 1.

#### Example 4

15       Powder of alumina hydrate particles (D) was prepared in the same manner as in Example 1 except that, in the aging step of Example 1, aging was performed at 100°C for 80 hr in place of 95°C for 80 hr.

With respect to the obtained alumina hydrate particles (D), the alkali metal content, ammonia content, average particle diameter and total pore volume were measured.

20       The results are listed in Table 1.

#### Preparation of water dispersion sol

Alumina hydrate particles (D) were dispersed in water, thereby obtaining a water dispersion sol having an  $\text{Al}_2\text{O}_3$  concentration of 20% by weight. The viscosity thereof was  
25       measured. Further, a water dispersion was prepared by

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dispersing alumina hydrate particles (D) so that the concentration in terms of  $\text{Al}_2\text{O}_3$  became 20% by weight, and the absorbance thereof was measured.

The results are also listed in Table 1.

5     Preparation of coating liquid for forming ink receptive layer

The above obtained alumina hydrate particles (D) were dispersed in water so that the solid concentration became 15% by weight. 100 parts by weight of this dispersion and  
10 37.5 parts by weight of a 10% by weight aqueous solution of polyvinyl alcohol were mixed together, thereby obtaining a coating liquid.

Preparation of recording sheet

The obtained coating liquid was applied onto a PET film  
15 by means of a bar coater, dried, and heated at  $140^\circ\text{C}$ . Thus, a recording sheet was obtained. The thickness of ink receptive layer was  $30\text{ }\mu\text{m}$ .

In the same manner as in Example 1, printing was performed on the obtained recording sheet and evaluated.

20     The results are also listed in Table 1.

Comparative Example 1

Powder of alumina hydrate particles (E) was prepared in the same manner as in Example 1 except that the temperature of hot air fed into spray drying zone was controlled at  $450^\circ\text{C}$

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and the temperature of gas discharged from the spray drying zone was controlled at  $180 \pm 10^{\circ}\text{C}$ .

With respect to the obtained alumina hydrate particles (E), the alkali metal content, ammonia content, average  
5 particle diameter and total pore volume were measured.

The results are listed in Table 1.

Alumina hydrate particles (E) were dispersed in water, thereby obtaining a water dispersion sol having an  $\text{Al}_2\text{O}_3$  concentration of 20% by weight. The viscosity thereof was  
10 measured. Further, a water dispersion was prepared by dispersing alumina hydrate particles (E) so that the concentration in terms of  $\text{Al}_2\text{O}_3$  became 20% by weight, and the absorbance thereof was measured.

The results are also listed in Table 1.

15 Preparation of coating liquid for forming ink receptive layer

The above obtained alumina hydrate particles (E) were dispersed in water so that the solid concentration became 15% by weight. 100 parts by weight of this dispersion and  
20 37.5 parts by weight of a 10% by weight aqueous solution of polyvinyl alcohol were mixed together, thereby obtaining a coating liquid.

Preparation of recording sheet

The obtained coating liquid was applied onto a PET film  
25 by means of a bar coater, dried, and heated at  $140^{\circ}\text{C}$ . Thus,

10070110 022802

a recording sheet was obtained. The thickness of ink receptive layer was 30  $\mu\text{m}$ . In the same manner as in Example 1, printing was performed on the obtained recording sheet and evaluated.

5 The results are also listed in Table 1.

Comparative Example 2

Alumina hydrate particle

An alumina hydrosol was prepared in the same manner as in Example 1 and concentrated in vacuum at 50°C, thereby  
10 obtaining an alumina hydrosol of 15% by weight concentration.

Part of the alumina hydrosol was air dried, thereby obtaining powder of alumina hydrate particles (F).

With respect to the obtained alumina hydrate particles (F), the alkali metal content, ammonia content, average  
15 particle diameter and total pore volume were measured.

The results are listed in Table 1.

Preparation of water dispersion sol

Alumina hydrate particles (F) were dispersed in water, thereby obtaining a water dispersion sol having an  $\text{Al}_2\text{O}_3$   
20 concentration of 20% by weight. The viscosity thereof was measured. Further, a water dispersion was prepared by dispersing alumina hydrate particles (F) so that the concentration in terms of  $\text{Al}_2\text{O}_3$  became 20% by weight, and the absorbance thereof was measured.

25 The results are also listed in Table 1.

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Preparation of coating liquid for forming ink receptive layer

The above obtained alumina hydrate particles (F) were dispersed in water so that the solid concentration became 15% by weight. 100 parts by weight of the resultant alumina hydrosol and 37.5 parts by weight of a 10% by weight aqueous solution of polyvinyl alcohol were mixed together, thereby obtaining a coating liquid.

Preparation of recording sheet

10 The obtained coating liquid was applied onto a PET film by means of a bar coater, dried, and heated at 140°C. Thus, a recording sheet was obtained. The thickness of ink receptive layer was 30  $\mu\text{m}$ . In the same manner as in Example 1, printing was performed on the obtained recording sheet and evaluated. The results are also listed in Table 1.

Comparative Example 3

Preparation of alumina hydrate particle

While agitating 12.7 kg of an aqueous solution of sodium aluminate (concentration in terms of  $\text{Al}_2\text{O}_3$ : 3% by weight), 7.3 g of a 26% by weight aqueous solution of sodium gluconate was added thereto, and further 25 kg of an aqueous solution of aluminum sulfate (concentration in terms of  $\text{Al}_2\text{O}_3$ : 1.5% by weight) was added over a period of 12 min. Thus, an alumina hydrogel was obtained. At the time of preparation of the

alumina hydrogel, the liquid temperature of alumina hydrogel is 30°C and pH of the obtained alumina hydrogel is 10.2. Thereafter, the agitation was discontinued, and the alumina hydrogel was aged at 30°C for 90 min.

5       The formed alumina hydrogel was separated by filtration, and satisfactorily washed with 1.5% aqueous ammonia. The amounts of alkali and sulfate radicals remaining in alumina hydrogel were 0.022% by weight in terms of  $\text{Na}_2\text{O}$  (on dry basis) and 0.12% by weight in terms of  $\text{SO}_4$  (on dry basis),  
10       respectively, based on the weight of  $\text{Al}_2\text{O}_3$ . Water was added to the washed alumina hydrogel so as to adjust the concentration in terms of  $\text{Al}_2\text{O}_3$  to 5.0% by weight. Subsequently, 15% aqueous ammonia was added so as to adjust the pH value to 11.2, and, under slow agitation, aging of  
15       alumina hydrogel was performed at 60°C for 10 hr.

During the aging, the pH value thereof was maintained at 11.2 by adding 15% aqueous ammonia.

Acetic acid was added at 95°C in an amount of 15.5% by weight based on the weight of  $\text{Al}_2\text{O}_3$ , agitated for 3 hr,  
20       and cooled to 35°C. Pure water was added, thereby obtaining an alumina hydrosol having a concentration in terms of  $\text{Al}_2\text{O}_3$  of 5.0% by weight.

The thus obtained alumina hydrosol was charged into a spray dryer, and spray drying was performed while  
25       controlling the temperature of hot air fed into spray drying

zone at 250°C and controlling the temperature of gas discharged from the spray drying zone at  $100 \pm 10^\circ\text{C}$ . Thus, powder of alumina hydrate particles (G) was obtained.

With respect to the obtained alumina hydrate particles (G), the alkali metal content, ammonia content, average particle diameter and total pore volume were measured.

The results are listed in Table 1.

#### Preparation of water dispersion sol

Alumina hydrate particles (G) were dispersed in water, thereby obtaining a water dispersion sol having an  $\text{Al}_2\text{O}_3$  concentration of 20% by weight. The viscosity thereof was measured. Further, a water dispersion was prepared by dispersing alumina hydrate particles (G) so that the concentration in terms of  $\text{Al}_2\text{O}_3$  became 5% by weight, and the absorbance thereof was measured.

The results are also listed in Table 1.

#### Preparation of coating liquid for forming ink receptive layer

The above obtained alumina hydrate particles (G) were dispersed in water so that the solid concentration became 15% by weight. 100 parts by weight of this dispersion and 37.5 parts by weight of a 10% by weight aqueous solution of polyvinyl alcohol were mixed together, thereby obtaining a coating liquid.

#### Preparation of recording sheet

The obtained coating liquid was applied onto a PET film by means of a bar coater, dried, and heated at 140°C. Thus, a recording sheet was obtained. The thickness of ink receptive layer was 30  $\mu\text{m}$ . In the same manner as in Example 5 1, printing was performed on the obtained recording sheet and evaluated. The results are also listed in Table 1.

10070110-022802

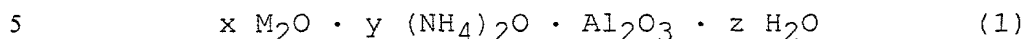


Table 1

	Alumina hydrate particle					Hydrate dispers-ion sol		Ink receptive layer			
	content of $M_2O$ $Al_2O_3$ $\times 10^{-4}$	content of $(NH_4)_2O$ $mol/mol$ $Al_2O_3$ $\times 10^{-4}$	average particle diam. $(\mu m)$	total pore volume $(ml/g)$	pore volume (15-30 nm) $(ml/g)$	viscosity conc. 20 wt. % (cP)	absorbance conc. 20 wt. %	reflect-ion den-sity	anti-blotting	drying speed	water resista-nce
Example 1	3.5	2.8	0.05	0.91	0.50	100	0.82	1.4	Excellent	Excellent	Excellent
Example 2	19.4	15.6	0.06	0.80	0.30	1490	1.18	1.3	Good	Excellent	Excellent
Example 3	10.0	0.5	0.06	0.82	0.41	135	0.95	1.3	Excellent	Excellent	Excellent
Example 4	12.8	3.9	0.06	1.20	0.71	57	1.25	1.4	Excellent	Excellent	Excellent
Comp.Ex. 1	4.6	3.0	0.30	0.45	0.20	4500	2.80	1.1	Poor	Poor	Poor
Comp.Ex. 2	30.0	155.0	0.50	0.51	0.21	8400	3.10	1.0	Poor	Poor	Poor
Comp.Ex. 3	3.5	25.0	0.03	0.31	0.10	6500	1.57	1.0	Poor	Poor	Poor

## CLAIMS

1. Alumina hydrate particles having a composition represented by the general formula:



$$2 \times 10^{-4} \leq x \leq 25 \times 10^{-4}$$

$$0.1 \times 10^{-4} \leq y \leq 20 \times 10^{-4}$$

$$0.6 \leq z \leq 2.5$$

wherein M represents an alkali metal; when the alkali  
10 metal is in the form of  $M_2O$ , x is the number of moles thereof per mol of  $Al_2O_3$ ; when ammonia is in the form of  $(NH_4)_2O$ , y is the number of moles thereof per mol of  $Al_2O_3$ ; and z is the number of moles of hydration water ( $H_2O$ ) per mol of  $Al_2O_3$ ,

15 said alumina hydrate particles having:  
an average particle diameter of 0.02 to 0.2  $\mu m$ ,  
a total pore volume of 0.5 to 1.5 ml/g, and  
a volume of pores whose diameter is from 15 to 30 nm ranging from 0.3 to 1.0 ml/g.

20

2. A process for producing alumina hydrate particles, comprising the steps of:

neutralizing an aqueous solution of alkali metal aluminate or an aqueous solution of aluminum salt to thereby  
25 form an alumina hydrogel;

10070110 022802

separating the alumina hydrogel by filtration, and washing the separated alumina hydrogel with water and/or aqueous ammonia;

adjusting the pH value of the washed alumina hydrogel  
5 so as to fall within the range of 9 to 12, and heating the alumina hydrogel at 50 to 105°C to thereby effect aging of the alumina hydrogel;

adding an acid to the alumina hydrogel so that the alumina hydrogel is deflocculated into an alumina hydrosol;  
10 and

drying the alumina hydrosol.

3. An alumina hydrate particle dispersion sol comprising a dispersion of the alumina hydrate particles claimed in  
15 claim 1 in water.

4. The alumina hydrate particle dispersion sol as claimed in claim 3 having a viscosity of 50 to 2000 cP exhibited when the  $\text{Al}_2\text{O}_3$  has a concentration of 20% by weight.

20

5. The alumina hydrate particle dispersion sol as claimed in claim 3 or 4 having an absorbance (ABS) of 2.0 or less exhibited when the  $\text{Al}_2\text{O}_3$  has a concentration of 20% by weight.

10070110-022802

6. A coating liquid for forming an ink receptive layer,  
comprising:

alumina hydrate particles claimed in claim 1, and  
a binder,

5 both dispersed in water and/or an organic solvent.

7. A recording sheet with ink receptive layer, comprising  
a substrate sheet having an ink receptive layer formed  
thereon from the coating liquid for forming an ink receptive  
10 layer, claimed in claim 6.

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## ABSTRACT

Highly transparent alumina hydrate particles having a large pore volume, having a pore diameter which falls in a specified range and, when formed into a high-concentration dispersion sol, exhibiting a low viscosity are provided. Alumina hydrate particles having a composition represented by the general formula  $x M_2O \cdot y (NH_4)_2O \cdot Al_2O_3 \cdot z H_2O$  ( $2 \times 10^{-4} \leq x \leq 25 \times 10^{-4}$ ,  $0.1 \times 10^{-4} \leq y \leq 20 \times 10^{-4}$ ,  $0.6 \leq z \leq 2.5$ , M represents an alkali metal; when the alkali metal is in the form of  $M_2O$ , x is the number of moles thereof per mol of  $Al_2O_3$ ; when ammonia is in the form of  $(NH_4)_2O$ , y is the number of moles thereof per mol of  $Al_2O_3$ ; and z is the number of moles of hydration water ( $H_2O$ ) per mol of  $Al_2O_3$ ), the alumina hydrate particles having an average particle diameter of 0.02 to 0.2  $\mu m$ , a total pore volume of 0.5 to 1.5 ml/g, and a volume of pores whose diameter is from 15 to 30 nm ranging from 0.3 to 1.0 ml/g.

## Declaration and Power of Attorney For Patent Application

## English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled NOVEL ALUMINA HYDRATE PARTICLE, ALUMINA HYDRATE PARTICLE DISPERSION SOL, COATING LIQUID FOR FORMING INK RECEPTIVE LAYER AND SUBSTRATE WITH INK RECEPTIVE LAYER, the specification of which

(check one)

- ☒ is attached hereto.
- ☒ was filed on August 9, 2000 as  
Application Serial No. PCT/JP00/05334  
and was amended on \_\_\_\_\_  
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
<u>245496/1999</u>	<u>Japan</u>	<u>31/Aug./1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u>                    </u>	<u>                    </u>	<u>                    </u>	<input type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u>                    </u>	<u>                    </u>	<u>                    </u>	<input type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)  
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)  
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

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